

THE PREPARATION OF CYCLOPENTENONES
FROM LACTONES.

FORMATION OF TETRAHYDROINDANONES

BY

RUTH CHARLOTTE PIERLE

A.B., University of Cincinnati, 1945

A.M., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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ACKNOWLEDGMENT

The author wishes to express her sincere appreciation to Dr. Robert L. Frank for suggesting this study and for his continued interest, encouragement, and advice during its execution.

The author is also indebted to the University of Illinois for graduate assistantships and fellowships from 1945 to 1949.



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INTRODUCTION

Under the influence of acidic catalysts such as phosphorus pentoxide, γ -lactones related to valerolactone undergo cyclization to form substituted cyclopentenones (1). In the case of δ -lactones of the perhydrocoumarin type, the expected products of such cyclization are tetrahydroindanones. By studying the reaction of phosphorus pentoxide with several substituted perhydrocoumarins and the structures of the products obtained, information has been gained concerning the course of the cyclization and its usefulness as a synthetic method for such compounds. In order to make such a study, it was first necessary to devise a satisfactory synthesis of the perhydrocoumarins.

DISCUSSION

The perhydrocoumarins were prepared by catalytic hydrogenation of the sodium salts of β -(2-oxocyclohexane)propionic acid and its 1-, 3-, and 5-methyl analogs. Acidification of the reduced compounds resulted in spontaneous lactonization. The lactones were colorless liquids with a characteristic sweet odor similar to coconut.

Two general methods were employed for the synthesis of the cyclohexanonepropionic acids from cyclohexanones: Mannich base alkylation (2) and cyanoethylation (3).

In the Mannich procedure, the Mannich base methiodide of cyclohexanone or the appropriate methylcyclohexanone was treated with sodiomalonic ester to form the substituted malonic ester. Acid or alkaline hydrolysis gave β -(2-oxocyclohexane)-propionic acid or its 3- or 5-methyl analog.

Monocyanoethylation of cyclohexanone and the methyl-

cyclohexanones was obtained by use of a four-to-one molar ratio of ketone to acrylonitrile, with Triton B (40% aqueous benzyltrimethylammonium hydroxide) as catalyst. Alkaline hydrolysis of the nitriles gave β -(2-oxocyclohexane)propionic acid and the corresponding 1- and 5-methyl compounds.

These methods proved to be complementary in making available the various methylperhydrocoumarins. In cases where either reaction will give the desired product, cyanoethylation is the method of choice, since fewer steps are required, the over-all reaction time is less, and the yield is somewhat higher.

The cyclization reaction was carried out by adding the lactone to phosphorus pentoxide and warming gently at reduced pressure to initiate the strongly exothermic reaction. The product was removed as rapidly as possible from the black reaction mixture by distillation through a column.

The primary product of the cyclization of perhydrocoumarin was 4,5,6,7-tetrahydroindanone (4), a colorless liquid with a somewhat spicy odor. The position of the double bond was established by ozonolysis to form γ -ketoazelaic acid and its oxidation products, succinic and adipic acids.

A second compound, indan, was also isolated as a cyclization product of perhydrocoumarin. This hydrocarbon was presumably formed from the unsaturated ketone by a process involving enolization, dehydration, and aromatization.

The methylperhydrocoumarins were likewise converted by phosphorus pentoxide into tetrahydroindanones and indans. The products from 6-methylperhydrocoumarin were 5-methyltetrahydroindanone and 5-methylindan; 8-methylperhydrocoumarin yielded 7-methyltetrahydroindanone and 4-methylindan. 10-Methylperhydrocoumarin was converted entirely into 4-methylindan, with none of the intermediate ketone being isolated. The rearrangement in carbon skeleton may be explained as resulting from a Whitmore shift (5) of the neopentyl-like carbonium ion formed as the first intermediate in the cyclization reaction.

The mechanism of the acid-catalyzed cyclization of lactones is similar to that of the Friedel-Crafts acylation reaction, with carbonium ion attack on the double bond of the β -(1-cyclohexene)propionyl carbonium ion which is presumably the principal intermediate.

The tetrahydroindanones were characterized by physical constants, analyses, derivatives, and ultraviolet absorption spectra. The observed absorption maximum at approximately 236-237 $m\mu$ ($\log \epsilon = 3.93-4.09$) is characteristic of α,β,β -trialkyl- α,β -unsaturated cyclopentenones (6). The semicarbazones also showed strong ultraviolet absorption in the expected region of 261-276 $m\mu$ ($\log \epsilon = 4.22-4.32$).

The indans were identified by physical properties, analyses, and ultraviolet absorption spectra, which showed the series of sharp absorption bands between 260 and 280 $m\mu$ characteristic of 1,2-disubstituted benzenes. Further proof of structure was afforded by permanganate oxidation, by which indan, 4-methylindan, and 5-methylindan were converted, respectively, into phthalic, hemimellitic, and trimellitic acids.

The combined yield of ketone and hydrocarbon from the lactone was usually 60-70%. The relative amounts of the two products varied widely in successive trials. The reason for this variation is not apparent, but is probably related to the difficulty of obtaining reproducibility in the composition of the two-phase reaction mixture.

Although the over-all yields from the cyclohexanones are low, the above method may be useful for the synthesis of 4,5,6,7-tetrahydroindanones which are not readily available by other means.

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VITA

The author was born in Cincinnati, Ohio, on November 16, 1923. She attended the public schools of that city and was graduated from Walnut Hills High School in June, 1941. In September of the same year she entered the University of Cincinnati, from which she received the degree of Bachelor of Arts in June, 1945. The following October she entered the Graduate College of the University of Illinois, receiving the degree of Master of Arts in June, 1947.

The author was employed as a research assistant at the Tanners' Council Research Laboratory at the University of Cincinnati during the summers of 1944, 1945, and 1946. In 1945 she was the recipient of the Katherine Wills Coleman Fellowship awarded by the National Council of Mortar Board. From 1945 to 1948 she held teaching and research assistantships at the University of Illinois. Since September, 1948, she has held a University Fellowship.



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